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THERMAL CONTROL COATINGS AND DEGRADATION MECHANISMS

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SUBJECT: Thermal Control Coatings and Degradation Mechanisms
Case 620

DATE: February 20, 1969

FROM: J. Gillespie

ABSTRACT

Thermal control coatings can be classified according to their surface properties and application to the spacecraft. These classifications and examples of their use in spacecraft are discussed. Thermal control coatings are subject to degradation caused by vacuum and ultraviolet, solar protons, micrometeoroids, and contamination. These mechanisms and the current assessment of the importance of each are discussed. In low earth orbit ultraviolet degradation appears to be the primary natural means of degradation, particularly for paints. Contamination appears to be a potentially serious problem although little data are available.

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MEMORANDUM FOR FILE

INTRODUCTION

A radiation heat balance with the space environment is an important part of spacecraft temperature control. Since the radiation heat balance depends on the thermal radiation characteristics of the vehicle surfaces, it is important that radiation properties remain stable or predictable in the space environment. Unfortunately, the space environment and contamination can cause changes in surface characteristics, leading to inadequate temperature control. Degradation of α_S from .2 to .4 can cause an increase in radiator sink temperature by as much as 80°F. Therefore, it is important that surface coating degradation mechanisms and the magnitude of degradation be known in order to properly design a spacecraft. This requires experimental determination of surface coating degradation in the laboratory and during actual space flight, with correlation between the two sets of data.

Two experiments proposed for AAP-2, but not yet approved, will provide data on coating degradation and will enable correlation to be made between actual space flight and laboratory experiments. Experiment T031, sponsored by the Marshall Space Flight Center, consists of exposed sample coatings and a hand-held integrating sphere reflectance measuring unit. The exposed coatings will be mounted on the Airlock Module and the astronauts will measure degradation in space. The other experiment D024(1) is sponsored by the Department of Defense and consists of exposed coatings to be mounted beside those of T031. Both experiments involve retrieval and return to Earth of the exposed coatings for further analysis. It appears that the experiments would complement each other, since the Marshall experiment would involve measurements in space that would be valuable in correlating space flight and laboratory data.

Another thermal coating experiment M415, proposed for AAP, was designed to measure degradation effects on coatings during the pre-launch and launch environment. This experiment consisted of two panels containing coatings, each with 12 thermal sensors, mounted on the Saturn IB Instrument Unit of AAP-1. Unfortunately, the experiment has been cancelled since the stage will not go into orbit; and there are no definite plans to place M415 on another flight, for example AAP-2. It is not possible to obtain satisfactory temperature data without obtaining thermal stability in orbit.

The purpose of this memorandum is to describe the various types of coatings and the mechanisms that cause coating degradation.

THERMAL SURFACE COATINGS

Coatings can be classified according to their surface properties. Four classes of coatings exist according to surface properties. They are: solar reflector $\alpha_s/\varepsilon << 1$; solar absorber, $\alpha_s/\varepsilon >> 1$; flat reflector, $\alpha_s/\varepsilon \approx 1$ with low α_s; and flat absorber, $\alpha_s/\varepsilon \approx 1$, with high α_s. Values of α_s and ε for typical materials belonging to these classes are shown in Table I.(2)

Coatings may also be classified according to their application to the surface. The classifications are: flame-sprayed coatings, vacuum-deposited coatings, chemical conversion coatings, paints, and second surface mirrors.(3)(4) The application methods and some examples of their use will be discussed.

Flame-sprayed Coatings

Flame-sprayed coatings are powders that are heated in a flame-spray gun and hot-sprayed on the spacecraft surfaces. The first United States space vehicle, Explorer 1, had a flame-sprayed coating of Al_2O_3 applied in predetermined stripes to produce $\alpha_s/\varepsilon = .437$. The coatings were exposed to aerodynamic heating during launch, thereby imposing a design restraint upon the coating.

Vacuum-deposited Coatings

The vacuum-deposited coatings, both metals and dielectrics, represent one of the more expensive methods for obtaining surfaces with specific optical properties. Much of the expense is due to the necessity for large vacuum chambers and other coating facilities necessary to coat large rigid areas. Handling is also a major problem, as are corrosion protection (prelaunch environment) and the repairing of defects or handling scars. However, a wide range of distinct values of α_s and ε can be obtained with very close tolerance.

The Vanguard II space vehicle required an $\alpha_s/\varepsilon = 1.3$ with as low values for both quantities as possible. The selected coating was a multilayer, vacuum-deposited coating. The basic satellite shell was magnesium alloy, which was gold-plated. A 500 Å layer of chromium was deposited on the gold surface as a primer to promote adherence. The second layer was a 500 Å layer of silicon monoxide that served as a diffusion barrier between the third layer, a 1000 Å coating of aluminum, and the chromium layer. The aluminum layer provided high reflectance required for maximum visibility. The fourth layer was a 6000 Å layer of silicon monoxide.

Chemical Conversion Coatings

Almost all metal surfaces form a very thin, homogeneous, dielectric film. Usually, this film is an oxide of the parent metal and may even be monomolecular in thickness. Conversion coatings, in general, extend the thickness of this film by chemical conversion. Application requires a chemical bath, precleaning and rinsing baths, and exacting processing control for reliable and repeatable coatings.

The Echo II satellite was constructed of a 3-layer laminate; a .18-mil thick layer of aluminum on each side of a .35-mil thick mylar film. The 135-foot sphere had an approximate volume of 1 1/4 million cubic feet and a surface area of 57,300 square feet. The surface coatings used were "Alodine 401-41" and "Alodine 1206 S" proprietary solutions of Anchem Products, Inc. These coatings were amorphous, phosphate coatings on aluminum, originally developed as protective surfaces and paint primers for aluminum coated, steel wire fencing. The Echo II 3-layer laminate was produced in 54-inch wide strips; therefore the laminate could be pulled through the "Alodine" bath at a controlled rate to produce the coating thickness required.

Paints

Thermal control paints consist of a pigment, which can be either a dielectric or semiconductor, and a binder, which can be either a silicone or a silicate. Paints offer several advantages over other types of coatings; flexibility in use; absence of detrimental effect on the structure of the substrate material; possession of a wide variety of optical properties; low cost of production; ease of application and repair; and compatibility with a wide variety of substrates.

However, paints are generally more susceptible to ultraviolet degradation than other coatings. Most paints are applied by spraying and may require reapplication and curing.

The Explorer IX satellite was a rigid sphere 12 feet in diameter made of a 4-layer aluminum laminate. The desired α_s/ε was achieved by applying titania pigmented expoxy paint in a uniform polka dot pattern to 18 percent of the surface.

Two paints that have received extensive testing are Zinc Oxide/Methyl Silicon (S-13) and Zinc Oxide/Potassium Silicate (Z-93).[5,6,7] The (S-13) coating was used on the SM adapters and the instrument units of the Saturn I. The (Z-93) coating is used on the CM-SM radiator.

Second-Surface Mirrors

The second-surface mirror developed by Lockheed consists of silver vacuum deposited on a .008-inch thick wafer of high quality fused silica. This combination yields $\alpha_s = .05$ and $\varepsilon = .81$ at 295°K. The high reflectance to solar energy is a result of the second surface silver film, whereas the high ε is produced by the fused silica. The coating system, called the Optical Solar Reflector (OSR), has been shown to be stable in the space environment.

The OSR can be fabricated in a variety of shapes and sizes; however, the most common configuration presently in use is that of 25-mm to 38-mm squares. Larger sizes can be produced, but breakage during fabrication and handling lead to increased costs. The weight is roughly twice that of comparable white paint coatings. Individual OSR mirrors are typically applied to a spacecraft surface using an adhesive that is selected for its compatibility with the OSR materials. The OSR was used sucessfully on Lunar Orbiter and various Air Force spacecraft.

DEGRADATION MECHANISMS

Space environmental hazards which are most likely to affect the properties of coatings are: (1) vacuum $\sim 10^{-15}$ Torr; (2) solar ultraviolet photons; (3) solar protons; and (4) micrometeoroids. The most serious, particularly for paints, is the combination of vacuum and ultraviolet radiation. Solar protons do not appear to be a problem in low earth orbit (below 200 nautical miles). Even above 200 nautical miles solar protons do not appear to be as important as ultraviolet degradation. However, little is known about the combination of ultraviolet and solar proton degradation. It appears that a sophisticated analysis is required to separate the effects of the two mechanisms when both occur. Since experiments T021 and D024 are mainly concerned with ultraviolet degradation they would not be useful in determining the effects of the combination of ultraviolet and proton degradation.

Other man-made mechanisms occur that could present serious problems. Nuclear reactors and isotope generators can produce neutron and gamma radiation. These mechanisms will not be discussed in this memo. Other mechanisms are contamination and aerodynamic heating. Contamination includes pre-launch contamination and in-space contamination by urine dumps, rocket firings, etc.

Ultraviolet and Vacuum

Data on the ultraviolet degradation of coatings has been obtained in laboratory experiments and from spacecraft flights. Information obtained from spacecraft is based on temperature measurements, therefore, this information may not be truly representative of degradation of surface optical properties. There is need for actual reflectance and emittance measurements to be made of coatings in the actual space environment. There is need also for spectral data on coating degradation. Experiment T031 would provide actual measurements in the space environment and spectral data.

The increase in solar absorptance of titania-expoxy and titania-silicone coatings due to ultraviolet radiation is shown in Figure 1. This information was obtained from the OSO-I satellite.[8] Comparison between the predicted increase based on laboratory tests and actual flight test are shown in Figures 2 and 3. In the laboratory the lamps used often subject test specimens to ultraviolet radiation many times as intense as the sun. Therefore, comparison is made in equivalent sun hours of exposure.

Data obtained from the OV1-10 satellite is shown in Figure 4.[9] The solar absorptance as a function of orbital time is shown for five specimens. The low α_s and stability of the second surface mirror (OSR) is evident. PV-100 and 78B2 are rutile type (TiO or TiO_2) pigments with silicone type binders. The other two coatings are also paints.

Additional flight data can be found in Reference 6 (Pegasus) and Reference 10 (ATS-1). Ultraviolet degradation for various pigments obtained from laboratory data is shown in Table II.(11) In general, natural, mined minerals were less affected by ultraviolet irradiation in vacuum than synthetic laboratory chemicals. Exceptions were zinc compounds and tin oxide.

Another degradation mechanism caused by ultraviolet radiation is an increase in absorptance in the infrared range of the spectrum. This degradation is peculiar to certain zinc oxide paints and the paint will recover after exposure to oxygen. This phenomenon is called oxygen bleaching. The paint S-13 decreased in reflectance by about 35% at 2 μ after approximately 800 equivalent sun hours of ultraviolet irradiation in vacuum.(12) However, nearly total recovery occurs after two minutes exposure to the atmosphere. It is felt by some investigators that the oxygen atoms available in low earth orbit can prevent this degradation. However, the phenomenon is not completely understood and further data are required.

Solar protons

Solar proton sputtering was found to remove about 1 Å per year for copper and about half this rate for iron and oxides.(13) However, sputtering not only removes material but it also produces chemical effects. Oxides of the non-transition elements yellow slightly due to the loss of oxygen. Black CuO is first converted to red Cu_2O, then to a film of Cu. Fe_2O_3 is converted to Fe_3O_4, FeO, and Fe under impact. Tin and protons combine to produce SnH_4 resulting in a larger apparent sputtering rate. Solar proton sputtering appears to be a small effect in comparison to ultraviolet degradation. However, during violent solar storms the possibility exists that serious degradation problems will arise.

Micrometeoroids

The information available on degradation of coatings from micrometeoroids is limited. Merill(14) reported on an analytical model which was developed to predict the change in emittance of a surface caused by particle impact. Changes were small over long durations.

Discrepancies existed between the model and experimental results. Mirtich and Mark(15) conclude that if changes in surface optical properties of 50 per cent are allowable, only missions over 7 months long will be affected. In NASA SP-5014(3) dated 1964, the assessment is that impacts of micrometeoroids over a period of years are not likely to greatly affect satellite temperature coatings. However, considerably more research is needed to determine the degradation of thermal coatings exposed to micrometeoroids.

Contamination and Aerodynamic Heating

Degradation of surface thermal coatings by contamination is a potentially serious problem. Contamination can occur during the prelaunch environment and while in orbit. As a rule of thumb, the reflectance may be expected to decrease by 0 to 5% due to prelaunch environment.(16) This includes handling and exposure to atmosphere prior to launch. Contamination while in orbit may be due to urine dumps, rocket firings, etc. This type of contamination may cause serious degradation problems. Great care must be taken to reduce in-flight contamination to a minimum. Data are required to fully evaluate the degradation effects of contamination.

Aerodynamic heating during launch can cause coating degradation. Many spacecraft have been shrouded to protect the coatings during launch. However, in AAP, vehicles such as the SM and OWS are not shrouded. In tests conducted by Douglas using a MORL* launch profile the coating Z-93 degraded from .163 to .174 in solar obsorptivity.(16) Emissivity was unaffected. Degradation during launch is of short duration and its effects can be estimated fairly well.

CONCLUSIONS

Thermal coatings have been developed that have a wide range of surface properties and applications. Thermal coatings are subject to many degradation mechanisms. In many instances the physics of the degradation process are not well understood and little data are available. This reduces the accuracy of spacecraft thermal predictions and requires some conservatism in spacecraft thermal design. More flight data, especially reflectance measurements while in space, are necessary for the accurate prediction of thermal coating degradation. The proposed AAP-2 experiments #T031 and #D024 should provide valuable information on ultraviolet degradation in near earth orbit. These experiments would:

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*MORL - Manned Orbiting Research Laboratory

1. Determine the effects of near earth space environments on selected experimental thermal control coatings which have been extensively investigated in the laboratory.

2. Compare data obtained from measurements made in the space environment with measurements made in vacuum chambers.

3. Provide new insights into the mechanisms of degradation of thermal control coatings caused by actual space radiation.

An experiment that would also determine degradation caused by in-flight contamination would also be extremely valuable.

1022-JG-ep

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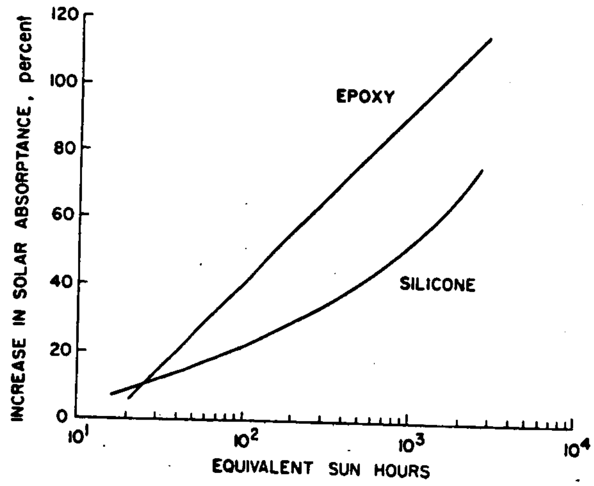

FIGURE 1—*Changes in solar absorptance of titania-epoxy and titania-silicone coatings due to ultraviolet radiation.*

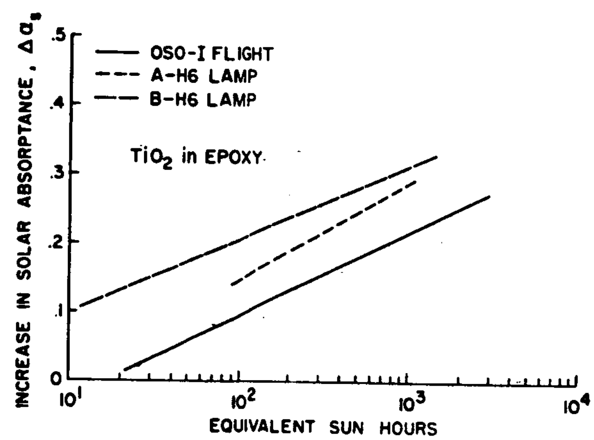

FIGURE 2—*Comparison of predicted increase in solar absorptance of titania-epoxy coating with in-flight results on the OSO-I satellite.*

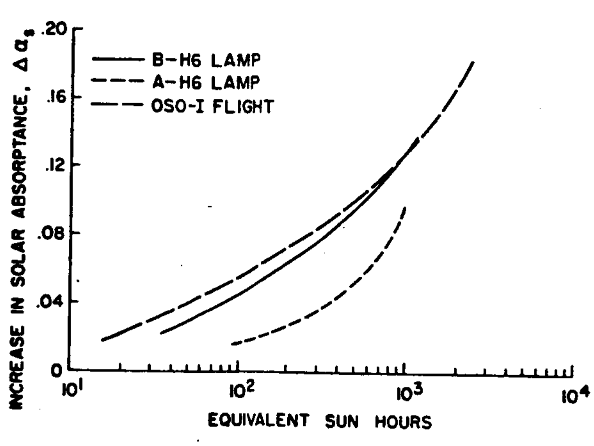

FIGURE 3—*Comparison of predicted increase in solar absorptance of titania-silicone coating with in-flight results on the OSO-I satellite.*

FIGURE 4

SOLAR ABSORPTANCE vs ORBITAL FLIGHT TIME

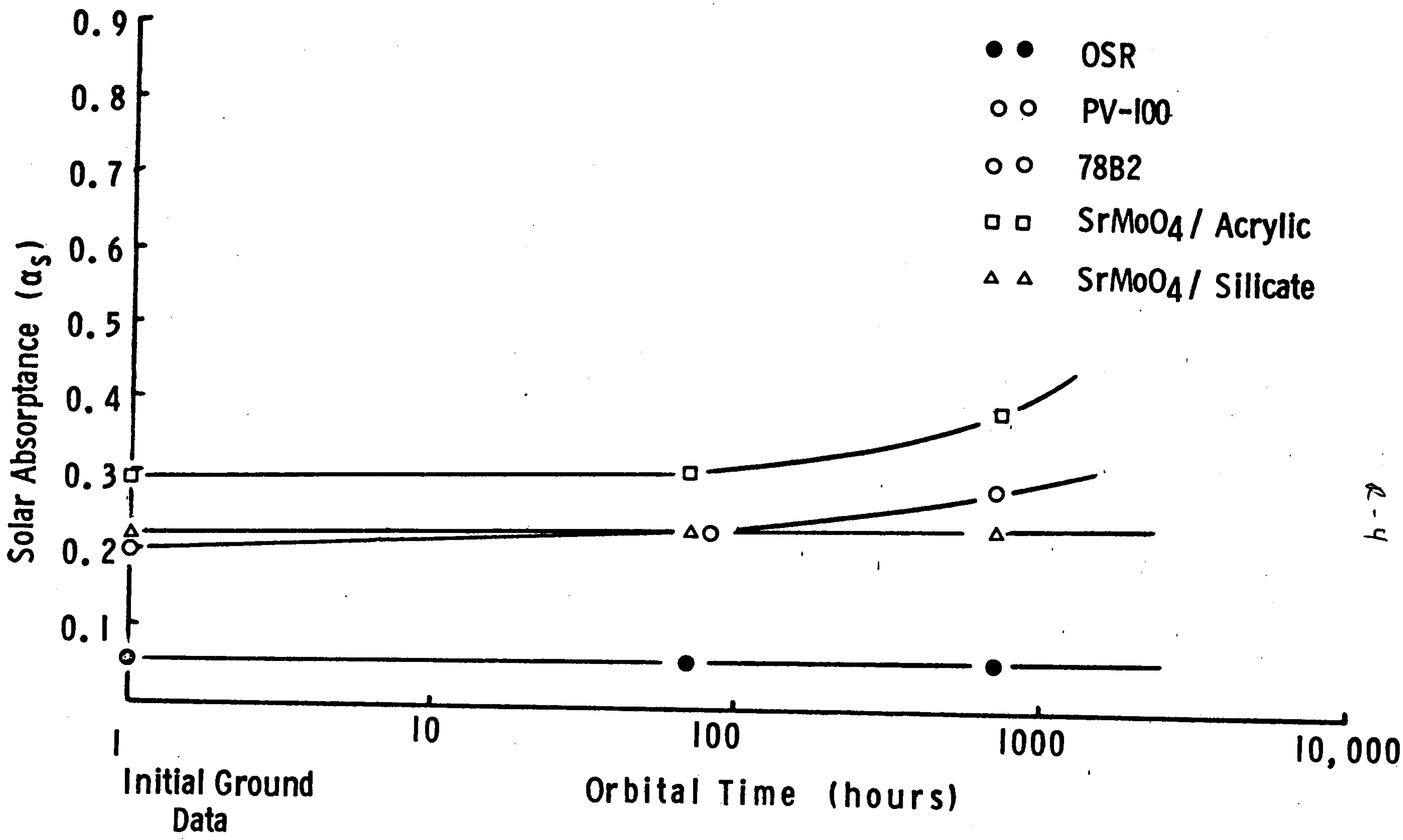

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TABLE I —*The Solar Absorptance (α_s) and Total Hemispherical Emittance (ϵ) at 500° R for Typical Materials Used for Spacecraft Thermal Control*

Material	Identification	α_s	500° R ϵ_H
Flat absorbers			
Rokide "C"	Flame-sprayed chrome oxide	0.90	0.85
Platinum black beryllium	Electrolytic deposited	.94	.80
Black acrylic paint	Sprayed to 5.0 mils	.94	.83
Black silicone paint	Sprayed to 5.0 mils	.89	.81
Flat reflectors			
Leafing Al acrylic	Sprayed to 3.0 mils	.30	.33
Nonleafing Al acrylic	Sprayed to 5.0 mils	.44	.36
Al silicone	Sprayed to 5.0 mils	.25	.26
Al silicate	Sprayed to 4.0 mils	.35	.37
Solar absorbers			
Aluminum	Polished and degreased	.39	.03
Gold over titanium with resin undercoat.	Polished	.30	.03
Beryllium	Chemically and mechanically polished	.44	.06
Inconel-X foil	Chemical polish	.62	.14
Solar reflectors			
Pigmented sodium silicate paint	Sprayed to 5.0 mils	.14	.91
Epoxy white paint	Sprayed to 5.0 mils	.26	.93
Sapphire	Coated on back side with silver	.10	.43
White plastic tape	Pressure-sensitive	.24	.89

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Table II - *Effect of Ultraviolet Irradiation in Vacuum on Optical Properties of Miscellaneous Inorganic Pigments*

Material	Designation and source	Exposure		Reflectance, %	
		ESH*	Solar factor	440 mμ	600 mμ
Al_2O_3	Alucer MC (alpha), Gulton Industries	0		100.0	100.0
		180	3	74.0	91.5
Al_2O_3	Alucer MA (gamma), Gulton Industries	0		93.5	90.0
		75	1.5	49.5	82.5
$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$	Ajax P kaolin, Georgia kaolin	0		73.0	84.5
		180	3	46.5	60.0
$Al_2O_3{\cdot}2SiO_2$	Ajax SC kaolin, Georgia kaolin	0		78.0	87.0
		200	3	65.0	81.0
$3Al_2O_3{\cdot}2SiO_2+SiO_2$	Molochite, Paper Makers Importing Co	0		84.5	86.5
		180	3	75.5	84.5
Sb_2O_3	National Lead Co	0		92.5	96.5
		75	1.5	36.5	50.0
$CaSiO_3$	Synthetic, Johns-Manville	0		86.0	90.0
		75	1.5	58.0	81.0
$CaSiO_3$	Wollastonite C-1, Cabot	0		92.5	94.5
		75	1.5	81.0	91.5
$MgAl_2O_4$	Spinel, Linde	0		97.5	97.0
		75	1.5	70.0	92.5
MgO	Reagent-grade powder, Mallinckrodt	0		98.5	98.5
		75	1.5	71.0	92.5
$MgSiO_3{\cdot}nH_2O$	No. 140 Alabama talc, Whittaker, Clark and Daniels.	0		89.0	92.0
		180	3	62.0	73.5
$2MgO{\cdot}SiO_2$	AlSiMag 243, American Lava	0		33.0	59.0
		1036	15	35.5	60.0
Magnesium trisilicate	USP, Mallinckrodt	0		97.5	99.0
		200	3	18.5	44.5
SiO_2	Ottawa Special, Ottawa Silica	0		88.5	92.5
		75	1.5	77.5	90.0
SiO_2	Diatomaceous earth, Dicalite WB-5, Great Lakes Carbon.	0		92.0	93.5
		180	3	87.5	93.0
SnO_2	CP, Fisher Scientific Co	0		88.0	90.0
		300	3	78.5	88.0
ZrO_2	CP, Titanium Alloy Mfg	0		92.5	97.0
		75	1.5	65.5	90.5
ZrO_2	Cubic, Titanium Alloy Mfg	0		88.0	95.5
		180	3	33.0	73.5
$ZrSiO_4$	Superpax, Titanium Alloy Mfg	0		86.5	92.5
		180	3	65.0	84.5
ZnS	Reagent grade, Matheson, Coleman, and Bell.	0		91.0	94.5
		75	1.5	89.0	94.0

*Equivalent sun-hours.

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